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### REVIEW OF THE COPROCESSING OF COALS AND HEAVY OILS OF PETROLEUM ORIGIN

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REVIEW OF THE COPROCESSING OF COALS AND HEAVY  
OILS OF PETROLEUM ORIGIN

by

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ABSTRACT

The present report reviews the various simultaneous cohydrogenation processes that are currently being recommended for coal and heavy oils of petroleum origin. The different coprocessing schemes are described, and the utilization of various catalysts and additives is discussed. A comprehensive bibliography of recent papers, patents and research reports is presented.

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ÉTAT ACTUEL DES RECHERCHES SUR L'HYDROGÉNATION SIMULTANÉE DU  
CHARBON ET DES HUILES LOURDES DÉRIVÉES DU PÉTROLE

PAR

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RÉSUMÉ

Ce rapport traite de l'hydrogénation simultanée du charbon et des huiles lourdes dérivées du pétrole. On y décrit différents procédés d'hydrogénation simultanée ainsi que l'utilisation de catalyseurs et d'additifs. La bibliographie contient de nombreuses références d'articles scientifiques, de brevets et de rapports techniques.

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## INTRODUCTION

The simultaneous hydrogenation of coal and heavy oils of petroleum origin is a new route for the hydrocracking of residual oils and bitumens, the liquefaction of coals and the removal of heteroatoms. An overview is given of the coprocessing of hydrocarbons based on information found in scientific papers, patents and research reports. In the first section, the pioneering work of Boomer and Saddington is presented. On-going projects at the Alberta Research Council as well as various coprocessing schemes such as the solvolysis and COIL processes are described in subsequent sections. The high-pressure solubilization of coal in residual oils is also discussed.

### EARLY WORK OF BOOMER AND SADDINGTON

In 1935, Boomer and Saddington pioneered the testing of solvents of petroleum origin for the liquefaction of lignite, subbituminous and bituminous coals from Alberta (1). Crude McMurray bitumen was mixed with an equal amount of Pincher Creek bituminous coal and heated at 425 or 450°C in rocking autoclaves from 3 to 8 h, initially under 7 MPa H<sub>2</sub> (measured at room temperature). A molybdic oxide catalyst was used (5 wt % coal). The products were separated by distillation and by extraction with ethyl ether. The conversion of coal to liquids and gases reached 50% at 425°C and bitumen hydrocracking took place simultaneously.

In tests with coal-tetralin mixtures, Boomer and Saddington developed two very effective catalysts: molybdic oxide and a mixture of 50 mol % ferric oxide and 50 mol % chromic oxide. According to these workers, the bimetallic catalyst gives a higher conversion of coal, while the molybdic oxide, a product distribution with less pitch.

### INVESTIGATIONS AT THE ALBERTA RESEARCH COUNCIL

Extensive research on the coprocessing of coal and bitumen is being done at the Alberta Research Council (ARC). Moschopedis, Speight\* and coworkers of the Coal Research Department (ARC) have investigated the liquefaction of Alberta bituminous and subbituminous coals in liquids of petroleum origin such as Suncor bitumen from the Athabasca oil sands deposit, Lloydminster heavy oil, Suncor coker gas-oil and maltenes from Suncor bitumen (2,3,4,5,6,7).

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These liquids differ from coal-derived oils in various ways (6). As shown in Table 1, the aromaticity is about 27-30 wt % for these heavy materials compared with more than 80% for the coal-derived anthracene oil. Furthermore, their average value of atomic hydrogen to carbon ratio is twice that of anthracene oil. However, their sulphur content, varying from 3.3 to 4.3 wt %, is high compared with less than 1 wt % for anthracene oil.

The coprocessing tests were performed in 300- and 1000-cm<sup>3</sup> autoclaves, with a feedstock ratio of 2.5 g of heavy oils per gram of powdered moisture- and ash-free (maf) coal (175 g hydrocarbon materials was used in a 1-L autoclave). The initial H<sub>2</sub> pressure in the reactor was set from 6.8 to 10 MPa; the vessel was then brought to a constant temperature, from 385°C to 420°C, for about 1 h. However, the slow heating rate of the autoclave (about 3.5-4.5°C/min) affected the accuracy of the reaction time since hydrocracking could already be taking place when the desired temperature was reached.

Moschopedis and coworkers investigated both the thermal cracking and the catalytic hydrocracking of coal-oil mixtures. Two catalysts were tested: Fe<sub>2</sub>O<sub>3</sub> (3 wt % maf coal) and cobalt-molybdenum oxides on alumina extrudates (about 10 wt %) (2,5,6,7).

The products were characterized according to the methods described in Table 2. The coal conversion was obtained by difference between the weight of solids in the autoclave before and after each run, the catalyst and mineral matter being excluded. Researchers at ARC have also done blank experiments by hydrocracking the liquid feedstock at the same operating conditions as the coprocessing runs in order to calculate the contribution of coal to the product distributions.

The results of the catalytic hydrocracking experiments indicate that coal conversion and product distribution are both affected by the type of coal and solvent and by the operating conditions.

When Ardley coal was processed with Lloydminster heavy oil at 400°C, 95% of the medium oil products boiled below 377°C compared with below 432°C for Judy Creek coal and 367°C for Fox Creek coal (7). However, further data are needed to correlate conversion and product distribution with the characteristics of different coals.

Lloydminster heavy oil and Suncor bitumen were found to be very effective solvents for the liquefaction of Wabamun B subbituminous coal at 400°C and 10 MPa  $H_2$ . Similar product distributions were obtained in both cases - 19-22 wt % naphtha, 24-25 wt % medium oils and 46-49 wt % oils boiling above 420°C (6).

In coprocessing, the gas products are not only comprised of light hydrocarbons,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$  and  $C_3H_8$  but also of  $CO_2$ , CO and  $H_2S$  because of the removal of oxygen and sulphur from the liquid products. Furthermore, the coke formation is usually minimized by the presence of a catalyst.

The ARC results suggest that the addition of coal leads mainly to an increase of the preasphaltene fraction in the products (6,7). However, by using maltenes derived from bitumen, a 35% increase in naphtha was observed while the volumes of extracts and medium oils increased only slightly. With coal-derived anthracene oil, the increase in liquid yield took place exclusively in the product fraction boiling above 420°C. The solvents of petroleum origin differed from anthracene oil in the product distribution of their blank experiments, as they formed more extracts and less medium oils.

Adding a small amount of  $H_2S$  (10 wt % coal) leads to a decrease in the production of volatile hydrocarbons (7). However, Moschopedis and coworkers did not observe any increase in the coal conversion due to the presence of  $H_2S$ .

#### COIL PROCESS

The COIL process for the catalytic hydrocracking of coal-oil mixtures is being developed at Hydrocarbon Research, Inc. (HRI) (8). This company already has to its credit the H-COAL process for coal liquefaction and the H-OIL process for heavy oil hydrocracking. Based on results obtained in bench-scale tests, HRI claims that coprocessing reduces, more than expected, the fraction of benzene insoluble products and the sulphur content of the liquids boiling above 204°C. These synergistic effects permit the operation of COIL at less severe conditions than processes such as bitumen hydrocracking and coal liquefaction. Microautoclave tests involving Western Canadian subbituminous coal and Lloydminster residual oils produced 10-30 vol %

naphtha and 15-35 vol % diesel fuel. The hydrogen required for COIL is produced by oxidation of the non-distillates and recovered from the gas outlet stream.

Chervenak and Johanson of HRI have processed, in an ebullated bed, mixtures of 1 part Illinois No. 6 coal with 1-2 parts Kuwait vacuum residual oils (93% of the materials boiling above 525°C) (9). The reactor temperature was 450°C and the hydrogen partial pressure, 15 MPa. A commercial cobalt-molybdenum catalyst was added to the feedstock. About 66 wt % of the products was made of distillate oils boiling below 525°C and having 4 carbon atoms or more, for a coal conversion of 94%. These results compare favourably with the distillate yield obtained in the hydrocracking of residual oils.

Part of the heavy distillate products can be recycled to keep the fraction of solids in the reactor from 10 to 25% of the total weight of hydrocarbons present.

#### ADDITIONAL CATALYSIS AND PROCESSES

Two patents were granted to Exxon Research and Engineering Company for the following oil-soluble coprocessing catalysts: phosphomolybdic acid and naphthenates of molybdenum, vanadium and chromium (salts of carboxylic acids derived from naphthenes).

In the first, Aldridge and Bearden describe experiments where a slurry of 50 wt % Athabasca bitumen and 50 wt % 74- $\mu$ m mesh Wyodak coal was heated in a 300-cm<sup>3</sup> autoclave at 440°C and 13.8 MPa H<sub>2</sub> for 60 min (10). By adding 837 ppm molybdenum as Mo naphthenate, based on the weight of the hydrocarbon feedstock, they increased the liquid yield by 20% to 84.3 wt % of the total carbon feed and decreased the coke formation by 60% to 8.8 wt %. The concentrations of iron, vanadium and nickel were drastically reduced to a combined metal content of 13 ppm compared with 423 ppm in the Athabasca bitumen.

In the second patent, tests were performed initially with a gas mixture containing 90-96 mol % H<sub>2</sub> and 4-10 mol % H<sub>2</sub>S, a 1:1 slurry of coal and bitumen was processed at 440°C and 13.8 MPa for 90 min in the presence of 200 ppm molybdenum (11). Blank experiments were also done by hydrocracking bitumen, in the absence of coal, at similar operating

conditions. By correcting the product distribution for the contribution of bitumen, these workers found that coal is predominantly converted to naphtha ( $C_4$ -193°C) and light distillates (193-343°C), accounting for 57 and 21 vol %, respectively, of the coal liquids, the remainder boiling above 343°C. These remarkable results are probably due to the high dispersion of the molybdenum catalyst, the relatively high reaction temperature and the long reaction time. However, this method of subtracting from the coprocessing products the contribution of bitumen to obtain that of coal, can be misleading because the reactivity of bitumen is assumed unchanged by the presence of coal.

This patent also describes a two-stage process in which bitumen is first hydrocracked for 1 h at 440°C and 13.8 MPa, before being hydrogenated with an equal amount of Wyodak coal for 30 min at the same conditions (11). Phosphomolybdic acid is the hydrocracking catalyst in both stages; the molybdenum concentration is about 200 ppm. A comparison of the two processes described in this patent indicates that the two-stage scheme produced more residual oils boiling above 540°C (17% vs. 13%) and more char (5.5% vs. 1.5%) than the single-stage process, due probably to shorter contact times between coal and bitumen. However, the hydrogen consumption is 12% lower in the two-stage process as suggested by the higher molecular weight products.

Unsupported catalysts, made of an organic metal complex or a metal salt of an organic acid, can hydrocrack a mixture of coal and crude petroleum oil at 390°C and 17.2 MPa, according to a patent owned by United Oil Products Inc. (12). The batch-autoclave tests described by Gatsis involve a 2:1 mixture of topped Boscan crude oil and Illinois No. 6 coal. The catalyst, 7 wt % molybdenum hexacarbonyl, is pretreated in situ at 300°C and 7 MPa of 10 mol %  $H_2S$  and 90 mol %  $H_2$ . The coal conversion reaches about 70%. The products are extracted with isopentane and toluene. The fraction containing the solids and the catalyst may be recycled in a new batch of slurried feedstock. Metals, such as nickel and vanadium are completely removed from the liquids (metal content less than 10 ppm); the heptane insoluble matters account for less than 0.3%.

Oxides of cobalt-molybdenum, nickel-molybdenum and nickel-tungsten, that are supported on silica-alumina, are suggested as catalysts by Rosenthal and Dahlberg for a two-stage coprocessing

scheme developed at Chevron Petroleum of California (13,14). In the first stage, coal is dissolved in an equal amount of heavy oils at 425-455°C and above 10 MPa H<sub>2</sub>. The effluent is then catalytically hydrocracked in a second stage at 340-400°C. Rosenthal and Dahlberg present data from coprocessing powdered River King coal with topped Kern River petroleum crude oil containing about 40% pitch. The dissolution, performed at 455°C and 16.5 MPa, is followed by hydrocracking at 400°C over a fixed bed of alumina pellets impregnated with 10 wt % Ni and 24 wt % W. The space velocity of the hydrocarbons is 1 h<sup>-1</sup> in the dissolver and 0.4 h<sup>-1</sup> in the reactor, respectively. Liquid products (65%) boil below 345°C and less than 5% above 540°C. The sulphur and nitrogen contents of the liquid fuels were less than 0.02 and 0.23 wt % respectively.

Titova and coworkers recently reported comparative studies involving different catalysts for coprocessing Russian coals and residual oils (boiling above 240°C) (15,16,17). The experiments were performed at 425°C for 2 h under initial hydrogen pressure of 5 MPa. The highest conversion, about 82%, was obtained using a catalyst made of coal particles impregnated with 0.2 wt % Mo<sup>+6</sup> [from a solution of (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>] and 0.75% Fe<sup>+3</sup> [from Fe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>]. In this case, 34% of the liquid products boiled below 300°C.

Kotowski described the production of gasoline and diesel fuels from processing bituminous coal with mazout (boiling at 348°C, Conradson number 9.05% and asphaltene content 2.93%), in the presence of Fe-Ni-Co-V catalyst (18). The initial oil to coal ratio was about 1.5 and the catalyst concentration, 3 wt % of the hydrocarbon feedstock. The hydrogenation was performed at 420-440°C and 9-11 MPa. About 12% of the liquid hydrocarbon products boiled from 40 to 200°C, 32% from 200 to 350°C, and 41% above 350°C.

#### COPROCESSING AT ATMOSPHERIC PRESSURE: THE SOLVOLYSIS PROCESS

The solvolysis process, for the dissolution of coal in asphalt or residual oils, is under development in Japanese laboratories (19,20). Two pilot plants, with respective throughputs of 1 and 36 t of hydrocarbon materials per day, are used for these solvolysis experiments.

In the first stage of the solvolysis process, 1 part coal is dissolved in 3 parts asphalt at 390°C and 100 kPa H<sub>2</sub> or N<sub>2</sub>. According

to Arita and coworkers, this temperature is optimum for the operation of the first stage because it minimizes the polycondensation of asphaltenes and the formation of gases (21,22). A residence time of less than 60 min is usually sufficient for coal dissolution.

The solvolysis pitch, i.e. the first-stage effluent from which solid matters are removed, is then hydrocracked over a catalyst to obtain liquid fuels. The second stage is kept at 400°C and below 20 MPa  $H_2$ . The pitch residence time is about 3 h. Oxides of nickel-molybdenum, cobalt-molybdenum and nickel-tungsten, impregnated on alumina, were tested by Japanese workers as hydrocracking catalysts (a pitch to catalyst ratio of 9.0). The Ni-Mo catalyst gave the best results. Zeolites and other commercial catalysts were also found suitable. Reactions of hydrodesulphurization and hydrodenitrogenation take place also, i.e., 60 to 90 % sulphur and 40 to 70 % nitrogen are removed from the liquids. Part of the liquid products can be recycled in the first stage to enhance the solubilization of coal and reduce the consumption of asphalt.

Gases, mainly methane, ethane and propane, account for less than 10% of the products; olefins are also present as well as  $H_2S$ . Carbon monoxide and carbon dioxide are formed when low-rank coals are liquefied. The solvolysis pitch is partly formed of normal paraffins with 15-23 carbon atoms.

Japanese workers have tested various additives for the first stage to improve the liquid yield; calcium carbonate was found to be quite effective. Disposable catalysts, like iron oxides, hydroxides and sulphides as well as mixtures of iron ore and sulphur, were also investigated; they all showed a positive effect on coal dissolution.

Coals having a carbon content from 80 to 85 wt % were experimentally found the most suitable for solvolysis. Highly-fusible coals are more easily converted than non-fusible ones. Leaching the coal with dilute acid enhances conversion. Similarly, thermal pretreatment of coals in the presence of ethylene and other olefins leads to an increase in the liquid yield. Japanese workers also observed that the dissolution of coal is improved when the asphalt is thermally treated.

Processes similar to coal solvolysis are described in Japanese patents. According to one of them, coal is liquefied by extraction with petroleum pitch that has been hydrogenated at high pressure over a

nickel-molybdenum catalyst (23). The coal conversion reached 88% when a mixture of 2 parts hydrogenated pitch and 1 part coal was heated at 370-390°C and 100 kPa for 60 min.

In a similar process developed by Osaka Gas Co. Ltd., small coal particles (50-10 000  $\mu\text{m}$  diam) are added to residuals from distillation of crude oil (24). The slurry is then heat-treated at 420°C and 1.5 MPa for 3 h to obtain liquid fuels.

Mitsubishi Chemical Industries Co. Ltd. also patented a solvolysis-type process (25,26,27). In the first stage, one part of low rank coal is heated at 400°C with 2 parts of asphalt-based oil, for 30 min. The effluent is then mixed with an equal amount of asphalt and heated at 400°C for 30 min. The final stage hydrogenates the pitch to fuel oil over a cobalt-molybdenum catalyst at 20 MPa for up to 3 h.

#### HIGH-PRESSURE COAL SOLUBILIZATION

A high-pressure version of the solvolysis process has been suggested by workers at Nippon Oil Co. Ltd. (28). Coal is liquefied by extraction at 400°C and 6 MPa with a solvent, prepared via a multi-stage treatment that includes pyrolysis of naphtha at 850°C, heat treatment at 350 and 400°C of the first-stage oil at 1.5 MPa for 2 h, followed by flash distillation and partial hydrogenation of the distillates at 300°C and 7 MPa  $\text{H}_2$ . A coal conversion of about 85% was reached with a feed mixture of 80 wt % oil and 20 wt % coal.

A two-stage process, similar to the Japanese high-pressure solvolysis, was also developed by Mobil Oil Corporation. Tests, described in various patents indicate that residual oils, from distillation of the effluent of a fluid catalytic cracker, (FCC), can be used as solvents in coal liquefaction (95% of these oils boil at 255-485°C) (29,30,31,32). Due to their high aromaticity, the FCC residual oils are very suitable for coal solubilization. Lignite and high-volatile bituminous coals, mixed with FCC residual oils, were 90%-converted into liquids at 400°C and 10 MPa  $\text{H}_2$ . No catalysts are used in this process.

Yan and Espenscheid from Mobil performed experiments in 300-cm<sup>3</sup> autoclaves under an initial  $\text{H}_2$  pressure of 101 kPa at 315-425°C (33). The final pressures, measured at reaction temperature, were as high as

6.9 MPa. In semi-batch experiments, a back-pressure regulator kept the autoclave pressure constant. The oils, asphaltenes and preasphaltenes were separated by extraction with pyridine and benzene. These workers claim that most of the FCC residual oils were recovered from the benzene solubles by precipitating the coal-derived liquids with a non-polar solvent, normal octane. Complete removal was obtained by a series of treatments with benzene and octane. Comparative studies were also made with a coal tar, boiling above 370°C.

The FCC residual oils were found to be good hydrogen donor solvents, suitable for coal liquefaction. They gave better quality products than the coal-derived solvent since their ratio of benzene solubles to insolubles was about 0.66 compared with 0.07 for coal tar. Results from semi-batch tests performed at 1.4 MPa, indicated that lower operating pressures decrease conversion and increase gas yields. On the contrary, high pressures enhance the production of liquids and the elimination of oxygen as CO<sub>2</sub> instead of H<sub>2</sub>O, reducing the H<sub>2</sub> consumption.

#### THEORETICAL COPROCESSING SCHEMES

The following Mobil Oil Corporation patents describe coprocessing schemes that have not been proven experimentally but are of interest.

In a two-stage process proposed by Yan, heavy oils, containing more than 75 wt % materials boiling above 371°C, are visbroken in a first stage and then used as solvent for liquefaction of lignite and subbituminous coals (34). To minimize coke formation, the two stages are operated at various temperatures to take advantage of differences in propensity for making coke, between heavy oils and coal. Suggested temperatures for stages 1 and 2 are 500°C and 425°C, respectively. Both stages are kept at about 4 MPa. The residence time of the heavy oils in stage 1 is less than 2 h to obtain a minimum conversion of 60%. Coal accounts for 30 wt % of the feedstock of stage 2. When most of the coal is liquefied, products are separated by solvent deasphalting and distillation. The hydrocarbon liquids are demetallized.

Rare-earth-exchanged zeolites are also proposed as coprocessing catalysts for the production of light olefins, distillates, light and heavy gas-oils and bottoms with a reduced metal content from a feedstock containing 60-80 wt % heavy oils (35). Hydrocracking is done at

427-524°C over an exchanged zeolite of type X, Y or ZSM-5 supported on a matrix of silica gel or co-gel of silica gel and a suitable metal oxide. The reaction pressure is set above 300 kPa and the catalyst concentration in the reactor is from 5 to 10 wt % of the coal-oil feedstock.

Yan also proposed the addition of fine particles of A-bituminous coal (50-2000  $\mu\text{m}$  diam) to enhance the visbreaking of heavy oils like Arabic light vacuum residuals (36). The reaction temperature is set at 425-510°C and the  $\text{H}_2$  partial pressure, as high as 13.6 MPa. The addition of steam during the process can be beneficial.

#### SUMMARY

The cohydrogenation of coal and heavy oils of petroleum origin produces larger volumes of hydrocarbon liquids than the liquefaction of coal. Therefore, less severe conditions of temperature and pressure are required in coprocessing. Even at atmospheric pressure, coal is partially soluble in asphalt. Furthermore, the coke formation is reduced because of lower reaction temperatures. Some of the coprocessing schemes described involve catalysts made of transition metals, such as nickel, cobalt, iron and molybdenum. However, the development of better catalysts and additives should be pursued to increase the production of high quality liquid fuels. Catalyst evaluation also requires a more detailed characterization of the products in terms of fractions of aromatic, cyclic and olefinic hydrocarbons.

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Table 1 - Analysis of feed stocks (6,33,37)

| Feed                                       | Composition (wt %) |       |      |       |      | H/C  | Aromaticity(%) |
|--------------------------------------------|--------------------|-------|------|-------|------|------|----------------|
|                                            | C                  | H     | S    | O     | N    |      |                |
| Anthracene oil                             | 92.10              | 5.35  | 0.96 | 1.13  | 0.55 | 0.70 | 80.1           |
| Forestburg Coal*                           | 70.76              | 4.28  | 0.59 | 22.55 | 1.82 | 0.73 |                |
| Wabamun coal<br>(Highvale Mine)*           | 73.3               | 4.6   | 0.4  | 20.7  | 1.0  | 0.75 |                |
| Illinois No.6<br>Coal *                    | 82.95              | 6.03  | 1.36 | 7.99  | 1.67 | 0.87 |                |
| FCC residual<br>Oils                       | 89.93              | 7.35  | 1.09 | 0.99  | 0.44 | 0.98 |                |
| Cold Lake<br>vacuum bottoms                | 78.6               | 9.3   | 5.5  | 5.9   | 0.60 | 1.42 |                |
| Lloydminster<br>heavy oils                 | 83.75              | 10.94 | 3.55 | 1.47  | 0.27 | 1.57 | 27.1           |
| Tar sand bitumen<br>(Athabasca<br>deposit) | 84.18              | 10.31 | 4.33 | 0.78  | 0.40 | 1.47 | 29.9           |
| Maltenes from<br>bitumen                   | 84.24              | 11.05 | 4.01 | 0.67  | 0.02 | 1.57 | 28.0           |

\*maf

Table 2 - Characterization of coprocessing products -  
Alberta Research Council (6)

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|                                      |                                                                                                                                                      |
|--------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|
| Gas products:                        | Gas chromatography analysis.                                                                                                                         |
| Naphtha-water fraction:              | Distillation at atmospheric pressure (20-195°C).                                                                                                     |
| Medium oils:                         | Distillation in vacuum (0.1-0.2 mm Hg) from 30 to 200°C. Boiling points equivalent to 195-420°C.                                                     |
| Heavy oils:                          | Extraction of the non-distillable residues with toluene, benzene and pentane; pentane solubles separated from resins on Fuller's earth with hexane   |
| Resins:                              | Extraction of the non-distillable residues with toluene, benzene and pentane; pentane solubles separated from heavy oils on Fuller's earth with THF. |
| Asphaltenes:                         | Extraction of the non-distillable residues with toluene, benzene and pentane; pentane insolubles.                                                    |
| Preasphaltenes:                      | Extraction of the non-distillable residues with toluene and pyridine; toluene insolubles and pyridine solubles.                                      |
| Unreacted coal, coke, ash, catalyst: | Extraction of the non-distillable residues with toluene and pyridine; toluene and pyridine insolubles.                                               |

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